Indian J. Phys **64A** (6), 464-468 (1990)

Isotope diffusion in zinc selenide

S Alfred Cecil Raj, N Lawrence, R Sebastian
Department of Physics, St. Joseph's College, Tiruchirapalli-620 002, India
and
K Ramachandran
School of Physics, Madurai Kamaraj University, Madurai-625 021, India

Received 30 November 1989, accepted 22 May 1990

Abstract : The results from the calculations of the Mean Square Displacements (MSD) of the neighbouring isotopic ions of both anion and cation vacancies by giving active role to the vacancy in zinc selenide are reported. The lattice Green's function and scattering matrix formalism have been applied for calculation of the MSD values for three temperatures 100 K, 200 K and 300 K. The results are compared with the experimental values of the perfect system. The calculated isotopic diffusion factor is found to be above 80% in anion case and around 60% in the cation case.

Keywords : Green's functions, lattice defect, resonant modes, MSD values.

PACS No : 63.20.Mt, 66.30.-h

1. Introduction

The nature of the displacements of a crystal defect, substitutional or interstitial or vacancy and those of neighbours around it have practical implications in the study of transport phenomena. The diffusion mechanism could be understood thoroughly if the displacement of the neighbours around a vacancy is known. Theoretical work regarding defect studies on II-VI semiconductors are limited. The authors (Alfred 1988) have already reported a high value of 80% isotopic diffusion effect for both anion and cation in ZnSe by giving passive role to the vacancy. It has been felt that whenever vacancy is created, the atoms surrounding the vacancy will relax from their respective equilibrium positions. Hence in this article the isotopic diffusion factor, calculated by giving active role to the vacancy, is reported along with the MSD values and resonant modes.

2. Theory

General theory discussed by Maradudin *et al* (1971) is used to calculate the MSD values of neighbours surrounding a vacancy as well as to work-out the resonant

modes. If the defect space consists of the defect as well as m-neighbours surrounding it, then the displacement of the defect space atoms are given by

$$U_1 = [I + gdI(I - gdI)^{-1}U]^{\circ}_1 \tag{1}$$

where U_1 is the column matrix representing the $3(m+1)$ components of the displacements, g is the Green's function matrix of the order of $3(m+1) \times 3(m+1)$, dI is the change in dynamical matrix of the order $3(m+1) \times 3(m+1)$ and U_1^0 is the displacement of the host crystal atoms.

To find the MSD of the defect space atoms, we have to get average amplitude over all the possible phonon modes. Thus we get an expression for the MSD at a particular temperature T as

$$\langle U_1^2(K, w)\rangle = (1/2)\int_0^{\infty} [U_1^2(K, w)/w] \coth (\hbar w/2K_B T)\, dw. \tag{2}$$

To calculate the isotopic diffusion factor the theory proposed by Flynn (1968) has been used here. Normally, an atom moves through the crystal by means of series of jumps, each jump involving an atom and an adjacent vacancy. The instantaneous relative displacement of the jumping atom and the neighbours obstructing the jump is defined as reaction coordinate X as

$$X = (U^{\alpha} - 1/n \sum U^{i}).\hat{X} \tag{3}$$

where U^{α} is the displacement of the diffusing atom along the α-direction, U^{i} is the displacement of the i-th atom in the ring of n-neighbours obstructing the jump and $\hat{X}$ is the unit vector along the jump direction. In terms of reaction coordinate, the atomic jump rate is given by

$$\Gamma = \frac{\left[\sum_{K,\lambda} w^2(K, \lambda)\ |\ X(K, \lambda)\ |^2\right]^{-\frac{1}{2}}}{\sum |\ X(K, \lambda)\ |^2} \exp\left[\frac{-X_0^2}{\sum_{K,\lambda} |\ X(K, \lambda)\ |^2}\right] \tag{4}$$

where X_0 is the critical value of the reaction coordinate, above which the jump materialises, $X(K, \lambda)$ is the contribution of the fluctuation for the reaction co-ordinate due to the (K, λ) mode, and $w(K, \lambda)$ is phonon frequency for the mode (K, λ).

The isotope effect is a measure of trace diffusion rate on the isotopic masses say M_1 and M_2 and is given by

$$\Delta K = \frac{(\Gamma_1/\Gamma_2 - 1)}{|\ (M_2/M_1)^{1/2} - 1\ |} \tag{5}$$

where Γ_1 and Γ_2 are the jump frequencies of the isotopes.

3. Method of calculation

When we consider an anion vacancy at the origin, there are four number of neighbours of cations at the positions given by ($\bar{1}/2$, 1/2, 1/2), (1/2, $\bar{1}/2$, 1/2), (1/2, 1/2, $\bar{1}/2$) and ($\bar{1}/2$, $\bar{1}/2$, $\bar{1}/2$) in units of the lattice constant. The matrices of g and dI are of order 15×15. The elements of Green's function matrices are worked-out using the modified Rigid Ion Model (Plumelle 1976) for 1000 wave vector points. $(I - gdI)$ is a complex matrix of order 15×15. In actual calculations, we have to take inverse of this matrix. But the time involved is very long, if we use the matrix as such. So, g and dI are block diagonalised into the irreducible representations

$$\Gamma_{15} = A_1 + E + F_1 + 3F_2, \tag{6}$$

using symmetry coordinates (Brice 1965). The MSD is computed from all the possible contributions of the phonon modes. The resonant modes are calculated for different irreducible representations mentioned above by evaluating the determinant of the matrix $(I - gdI)$.

4. Results and discussions

When a vacancy is created in the lattice, the atoms surrounding it, relax slightly. This will result a change in force constant values. An accurate calculation of the change in force constant values involve sophisticated computer facilities. The actual values of change in force constants have been calculated (Nerenberg 1980) for fluorites using HADES programme. It has been reported that the force constant parameters vary from 0.7 to 20%. So, as a first step, within our computer facility, we have calculated the MSD values with 5% relaxation, which lies with in the limit reported for fluorites (Nerenberg 1980). The calculated results of MSD values for both anions and cations surrounding a vacancy are arranged in Table 1, with the experimental (Talwar 1975) values for comparison. There is good agreement for anions. For the case of cations at 300 K, our result deviates slightly from the experimental results. This variation may be due to the assumption in the relaxation. A refined calculation can be done by accounting the actual relaxation.

Resonant modes have been calculated for various irreducible representations by giving 5% change in the force-constant values for anion vacancy. It is found that the resonant modes occur only for F_2 representation. The various $X(=w/w_{max})$ values at which the resonance occurs are arranged in Table 2. The values for passive role are also quoted in the same table for comparison. From the values presented in the table, it is found that the resonant modes are shifted with respect to X values. This shift may affect the result of MSD values as well as the related

parameters. There is neither experimental nor theoretical result available to verify the calculated modes. But the trend is similar to one obtained for HgTe system (Madhavan and Ramachandran 1989).

Table 1. Mean Square Displacement of both Zn ($<U^2>+$) and Se ($<U^2>-$) atoms in units of A^{o2} for a 5% change of force constant.

Temperature K	This calculation		Experimental	
	$<U^2>-$	$<U^2>+$	$<U^2>-$	$<U^2>+$
100	0.00568	0.0068	0.0031 (at 77° K)	—
200	0.01018	0.1173	—	—
300	0.01490	0.01745	0.0100	0.0117

The various isotopes of zinc and selenium and the corresponding isotopic diffusion factor and the pre-exponential factor of atomic jump frequency are

Table 2. Resonant modes due to anion vacancy in ZnSe.

Relaxation representation	5%	
	Passive	Active
F_2	0.028	0.912
	0.213	0.935
	0.308	0.979

arranged in Table 3. Our results of isotopic diffusion factors with passive role to the vacancy are also quoted in the table for comparison. It is found that the value

Table 3. Pre-exponential factor and isotope effect.

	Isotope pre-exponential factor $\times 10^{-14}$ rad/s		Isotope effect ΔK		
	Passive	Active	Passive	Active	
Zn^{68}	0.1429	0.1349	0.84	0.78	(68, 66)
Zn^{66}	0.1448	0.1365	0.74	0.84	(68, 64)
Zn^{64}	0.1462	0.1383	0.64	0.88	(64, 66)
Se^{82}	0.1426	0.1359	0.77	0.59	(78, 82)
Se^{80}	0.1439	0.1370	0.74	0.73	(80, 82)
Se^{78}	0.1454	0.1380	0.80	0.57	(78, 80)

(numbers within parentheses denote the isotopic masses).

of isotope diffusion factors reduced slightly when active role is given to the vacancy. This may be due to the shift in resonant modes for active role with respect to X values as discussed in the previous paragraph.

5. Conclusion

There are not much experimental results to justify our calculated values. However, our MSD values are agreable to the experimental results. Moreover, the pre-exponential factor of jump frequency is of the same order of the Debye frequency 0.251×10^{14} rad/sec of the perfect host crystal. These are the good indications for the success of our method of calculations. More experimental results are expected in this direction to compare our theoretical results.

Acknowledgment

One of the authors (RS) wishes to thank the University Grants Commission, New Delhi, for financial assistance.

References

Alfred Cecil Raj S, Sebastian R and Ramachandran K 1988 *Indian J. Pure Appl. Phys.* **26** 722

Brice K D 1965 *Phys. Rev.* **140** A1211

Flynn C P 1968 *Phys. Rev.* **171** 682

Madhavan Y and Ramachandran 1989 *Indian J. Pure Appl. Phys.* **27** 43

Maradudin A A, Montrol E W, Weis G H and Ipatova I P 1971 *Theory of Lattice Dynamics in Harmonic Approximation Suppl 3* (New York : Academic)

Nerenberg M A H, Haridasan T M, Govindarajan J and Jacobs P W M 1980 *J. Phys. Chem. Solids* **41** 1217

Plumelle P and Vandevyner M 1976 *Phys. Stat. Sol.* **b73** 271

Talwar D N and Agarwal B K 1975 *J. Phys.* **C8** 2043